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Thermal degradation behaviors and kinetics of biomass tar

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Abstract

The thermal degradation behaviors and kinetics of tar, which was gained from straw gasification, were studied at different heating rates (10K/min, 20K/min, 30K/min) under nitrogen atmosphere by thermogravimetric (TG) coupled with Fourier transform infrared spectrometer (FTIR). TG-DTG curves and the corresponding infrared spectrometers were analyzed. The model of pyrolysis kinetics for tar was established and the kinetics parameters of tar were also calculated. The results indicate that the pyrolysis of tar contains two stages, the evaporation stage and the decomposition stage. And both the stages can be expressed by first-order reaction. According to the infrared spectrometers, the pyrolysis products are mainly composed of water, CH_4, CO_2, CO, alkanes, alkenes, alcohols and esters. The physical and chemical processes of products during tar pyrolysis were analyzed in this paper. Theoretical guidelines for biomass tar pyrolysis are provided based on the insight gained from the experimental results.

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Key words: biomass; tar; pyrolysis; TG-FTIR; kinetics

Biomass gasification has drawn increasing attention since it can supplement fossil fuels and reduce greenhouse gas emissions. However, tar which is by-product during biomass gasification becomes major bottleneck when implementing this technology. For this reason, special effort must be done in understanding of kinetics and characteristics of biomass tar thermal degradation.

Up to now, few researchers have investigated the kinetics and products of tar pyrolysis and many of them focused on the analysis of pyrolysis characteristics and solving the kinetic parameters. Li[1] analyzed the TG/DTG data with and without dolomite catalyst and solved the kinetic parameters using Coats-Redfern and distributed activation energy models(DAEM). Jess[2] used tar model compounds to study the pyrolysis behavior and obtained the kinetic parameters by fitting the data. Tar which is derived from straw gasification was chosen as experimental sample in this paper, because straw is one of the common agriculture wastes in northern part of China. TG coupled with FTIR was adopted to obtain information on

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tar degradation behavior and products under three different heating rates(10, 20, 30 K/min). Guidelines for tar pyrolysis mechanism are provided based on the insight gained from these results.

Nomenclature

E	apparent energy activation
A	pre-exponential factor
R^2	correlation coefficient
α	the weight loss rate
β	the heating rate

Materials and method

Tar samples (from straw gasification) were collected from Tianjin Daming Hengyun Renewable Energy Technology Company. The samples were analyzed by TG-FTIR (STA449F3JupiterTENSOR27). The amount of every sample was approximately 10mg. Crucibles were made of Al_2O_3. The flow rate of carrier gas was 20mL/min. The heating rates were 10 K/min, 20 K/min, 30 K/min and the programmed temperature were 293~1123K. The pipe connecting the TGA and FTIR was heated to 473K and the detector was used with a spectrum range of 600~4000cm^{-1}.

Results and discussion

1.1. Tar pyrolysis characteristics

TG and DTG curves of tar which is derived from straw gasification at different heating rates are shown in Fig. 1 and 2. According to DTG curve of heating rate 20K/min, tar degradation can be divided into two stages. The first stage (temperature range of 323~393K) is volatile process for light components of low boiling points. And the weight loss rate for this stage is 62 wt%. The second stage (temperature higher than 393K) consists of the thermal cracking stage of heavy components and volatile process of components with high boiling points. And its weight loss rate is 29 wt%.493K corresponds to the peak of maximum weight loss. When the temperature is beyond 853K, tar weight loss tends to be slow, even to stop. This phenomenon is owing to a small amount of coke generation during this process. The total weight loss rate of tar pyrolysis with heating rate 20K/min reaches to 91%. The other two heating rates also have these similar trends. In addition, all TG-DTG curves have the offset trend to higher temperature with the increasing of heating rates, due to the hysteresis of heat transfer for tar.

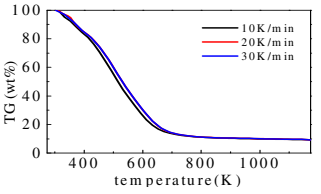

Fig.1. TG curves with different heating rates

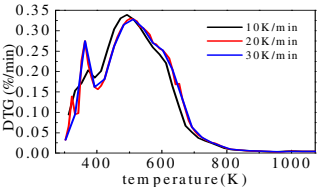

Fig. 2. DTG curves with different heating rates

1.2. Tar FTIR analysis

The spectrum of gas products in the process of tar thermal degradation (heating rate of 293K/min) are presented in Fig. 3. At the first stage low boiling points components are volatilized, such as benzene compounds (770~730cm^{-1}), aromatic ether (1285~1240cm^{-1}), alkanes and olefins (2990~2850cm^{-1}, 3100~3000 cm^{-1}).When temperature reaches 493K, the amount of gas production achieves to the maximum. Some researchers also observed this similar phenomenon[3]. The gas production contains light organics, such as acetic acid (1846~1710 cm^{-1}), ethanol (3050~2800 cm^{-1}, 1180~943 cm^{-1}), acetone (1800~1600 cm^{-1}, 1400~1107 cm^{-1}), and fixed gases, like CH_4 (3200~2850 cm^{-1}), CO_2 (2400~2260 cm^{-1}) and H_2O (3964~3500 cm^{-1})[4-5]. CO_2 comes from the decomposition of carboxyl. And CH_4 derives from the cleavage of fatty chains and aromatic side chains with methyl groups. H_2O is mainly from dehydration reaction and the side-strand breaking of phenols and alcohols. As temperature increases, more and more heavy components start cracking and small molecular gases are released. As shown in Fig. 3, some CO begins to generate at 1033K. The generation of CO depends on the decomposition of quinone ether and the oxygen-containing heterocyclic ring. In addition, CO_2 reacts with the coke could also produce CO.

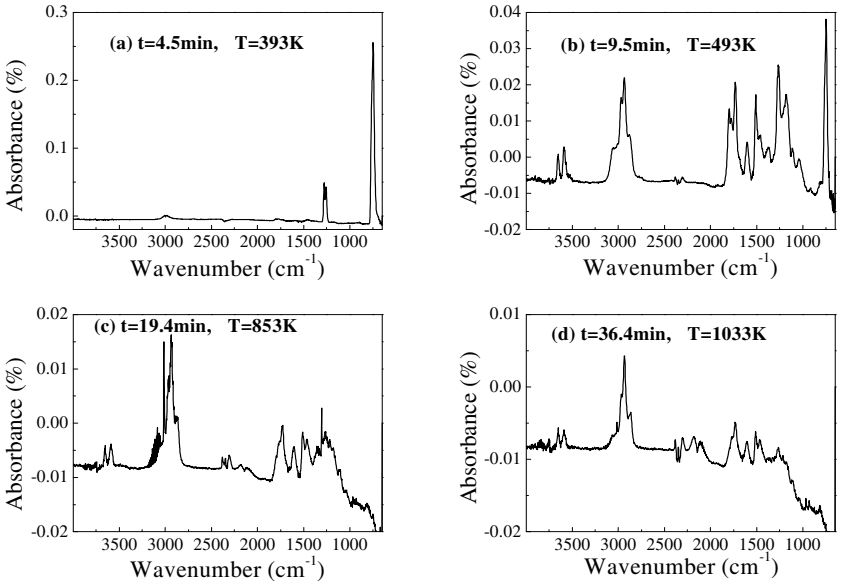

Fig. 3. Typical FT-IR spectrum of gas product releasing from tar pyrolysis

1.3. Kinetic analysis of tar pyrolysis

According to Arrhenius equation, the kinetics of tar pyrolysis can be expressed by Equation (1).

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

According to the approximate expression of Coats-Redfern method, Equation (1) can be integrated as follows,

$$\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right)=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \qquad n=1 \tag{2}$$

$$\ln\left(-\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right)=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \qquad n\neq 1 \tag{3}$$

Through fitting the data, N=1 is obtained, which means the reaction could be expressed by the first reaction order. A series of E and A values could be calculated. Detailed kinetic parameters are shown in Table 1.

Table 1. Kinetics parameters of tar pyrolysis

Sample	Heating rate (*K/min*)	Temperature range (*K*)	Reaction order	E (*kJ/mol*)	A(min^{-1})	R^2
Tar	10	298~403	1	16.584	7.163	0.992
		403~1043	1	10.540	0.726	0.972
	20	298~393	1	26.900	139.705	0.983
		393~1023	1	10.915	0.396	0.982
	30	298~393	1	26.946	413.079	0.983
		393~1083	1	11.156	1.097	0.982

Conclusions

Tar pyrolysis could be divided into two stages. The first stage is the volatilization process of light components of low boiling points. And the second stage is the pyrolysis process of heavy components. During the second process, components of high boiling points volatiles and some components which has weak thermal stability decomposes. Pyrolysis gases are consisted of small hydrocarbon molecules and small molecular gases. Both the two stages could be described by the first order reaction. Moreover, the heating rates have influence on the activation energy of the tar pyrolysis. At the same heating rate, the activation energy of tar pyrolysis decreases with the temperature increasing. However, in the condition of different heating rates at the same stage, the activation energy of tar pyrolysis increases with the heating rate increasing.

Acknowledgements

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